WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C02F 1/50	A1	(11) International Publication Number: WO 97/43215
COME 1/30		(43) International Publication Date: 20 November 1997 (20.11.97)
(21) International Application Number: PCT/US9 (22) International Filing Date: 16 May 1997 (1		DE DK ES EL ED GR GR IE IT LLI MG NE DE
(30) Priority Data: 08/648,972 17 May 1996 (17.05.96)	U	Published S With international search report.
 (71) Applicant: BIO-LAB, INC. [US/US]; P.O. Box 1489, 1 GA 30031-1489 (US). (72) Inventors: MITCHELL, Presley, K.; 3305 Pebble Hil Marietta, GA 30062 (US). PERRY-MURPHY, I J.; 704 Brookstone Circle, College Park, GA 3034 LINES, E., LeRoy; 5630 Eden Roc Lane, Atlanta, GA (US). SHELOR, Susan, M.; 6280 Murets Road, Alp GA 30202 (US). (74) Agents: THOMAS, Timothy, N. et al.; Woodard, E. Naughton, Moriarty & McNett, Bank One Center/Suite 3700, 111 Monument Circle, Indianapolis, IN (US). 	I Drive Delores 9 (US) A 30342 sharetta mhardt, Tower, 46204	
54) Title: METHOD FOR SANITIZING SWIMMING POO	DLS A	ND RECIRCULATING WATER SYSTEMS

(57) Abstract

A method of treating the water of a swimming pool equipped with a skimmer basket by placing bromochlorodimethylhydantoin in the skimmer basket and a cationic polymer in the pool.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL AM AT AU AZ BA BB BE BF BG BJ BR CCF CG CH CCI CM CN CU CZ DE DK EE	Albania Armenia Austria Austria Australia Azerbaijan Bosnia and Herzegovina Barbados Belgium Burkina Faso Bulgaria Benin Brazil Belarus Canada Central African Republic Congo Switzerland Côte d'Ivoire Cameroon China Cuba Czech Republic Germany Denmark Estonia	ES FI FR GA GB GE GH GN GR II IS IT JP KE KG KP LC LL LR	Spain Finland France Gabon United Kingdom Georgia Ghana Guinea Greece Hungary Ireland Israel Iceland Italy Japan Kenya Kyrgyzstan Democratic People's Republic of Korea Republic of Korea Republic of Korea Kazakstan Saint Lucia Liechtenstein Sri Lanka Liberia	LS LT LU LV MC MD MG MK ML MN MR MW MX NE NL NO NZ PL PT RO RU SD SE SG	Lesotho Lithuania Luxembourg Latvia Monaco Republic of Moldova Madagascar The former Yugoslav Republic of Macedonia Mali Mongolia Mauritania Malawi Mexico Niger Netherlands Norway New Zealand Poland Portugal Romania Romania Russian Federation Sudan Sweden Singapore	SI SK SN SZ TD TG TJ TM TR TT UA UG US UZ VN YU ZW	Slovenia Slovakia Senegal Swaziland Chad Togo Tajikistan Turkmenistan Turkey Trinidad and Tobago Ukraine Uganda United States of America Uzbekistan Viet Nam Yugoslavia Zimbabwe	
--	--	--	---	---	---	--	--	--

METHOD FOR SANITIZING SWIMMING POOLS AND RECIRCULATING WATER SYSTEMS

FIELD OF THE INVENTION

The present invention relates generally to methods for sanitizing recirculating water systems, and more particularly to a method of using N-halogenated hydantoins to sanitize swimming pools.

BACKGROUND OF THE INVENTION

N-halogenated hydantoins such as bromochlorodimethylhydantoin have long been recognized as effective
disinfectants for circulating water systems. For example,
in 1964 Paterson disclosed the use of
bromochlorodimethylhydantoins as disinfectants for swimming
pool water after recognizing that organo-bromo-chlorinated
compounds appeared to have enhanced bacteriacidal activity
when compared to disinfecting compositions containing
bromine or chlorine alone. See, U.S. Patent No. 3,147,219.

Unfortunately, it has also long been recognized that there are significant problems associated with effectively delivering N-halogenated hydantoins to swimming pool water. Paterson initially studied and "solved" the problem with respect to bromochlorodimethylhydantoin in U.S. Patent No. 3,412,021, issued in 1968, by suggesting that bromochlorodimethyl- hydantoins should be delivered as a solid agglomerate disposed in a reservoir "so that the surface area of the agglomerates exposed to the impure water is held substantially constant." See, U.S. Patent No. 3,412,021 at col. 3. lines 44-51.

20

25

-2-

In recognition of the accepted view that N-halogenated hydantoins such as bromochlorodimethylhydantoins should be delivered by placing an agglomerate of the disinfectant in a reservoir constructed so that a constant surface area of the agglomerate is exposed to the water, the prior art developed the use of separate "brominator" chemical dispensing devices to dispense the N-halogenated hydantoin product. Examples of such "brominators" include the Di-Halo® Automatic Swimming Pool Disinfecting System and the Aquabrome® Brominator.

10

15

20

25

Certain disadvantages are known to be associated with brominator dispensing systems. For example, swimming pools in geographical areas prone to freezing temperatures must winterize all plumbing equipment, including the brominator chemical dispensing device. This is a time consuming process, and may subject the pool owner and/or operator to unnecessary chemical exposure when purging the brominator of agglomerated or tableted hydantoin. In addition, the consumption rate of dimethylhydantoin is greater than necessary when brominator units are used.

A need therefore exists for a method of disinfecting swimming pools with N-halogenated hydantoins such as dihalodimethylhydantoins, whereby disinfectant consumption is reduced, the need for associated plumbing and equipment is eliminated, and superior water quality is maintained. The present invention addresses that need.

10

SUMMARY OF THE INVENTION

Briefly describing one preferred embodiment of the present invention, there is provided a method of treating the water of a swimming pool by putting an agglomerate of bromochlorodimethylhydantoin in the skimmer basket, and a cationic polymer in the pool, and allowing a substantial portion of the agglomerate to dissolve before replenishing the supply of agglomerate in the skimmer basket.

One object of the present invention is to provide an improved method of delivering N-halogenated hydantoin to swimming pool water.

Another object of the present invention is to provide an improved method of delivering BCDMH to swimming pool water.

Further objects and advantages of the present invention will be apparent from the following description.

-4-

DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the illustrated device, and such further applications of the principles of the invention as illustrated therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

5

10

15

25

30

One preferred embodiment of the present invention relates to an improved method of effectively providing bromochloro-5,5- dimethylhydantoin ("BCDMH" or bromochloro-5,5-dimethyl-2,4- imidazolidinedione) to swimming pool water. In the prior art, a special "brominator" dispensing apparatus was understood to be required to provide a bed of BCDMH agglomerate that contacts the pool water as it is pumped through the pool filter. 20 another preferred embodiment other N-halogenated hydantoins are used.

The present invention eliminates the requirement to have a separate chemical dispensing device for delivering dihalodimethylhydantoins to the pool. Instead, one preferred embodiment of the present invention effectively delivers bromochlorodimethylhydantoin to swimming pool water by placing one or more pucks of BCDMH in the pool's skimmer basket and replacing the pucks only after they have substantially dissolved. With this method the surface area of the BCDMH is not constant as it would be with prior art methods.

In another preferred embodiment, bromochlorodimethylhydantoin is effectively delivered by placing pucks of BCDMH in the skimmer basket in conjunction with the addition of a

20

25

cationic polymer to the pool water. Here too, the surface area of the BCDMH is not constant as it would be with prior art methods.

In a third preferred embodiment, an N-halogenated

composition is added to a recirculating water system by contacting the recirculating water with solid pieces of the N-halogenated composition, wherein the surface area of the N-halogenated composition is allowed to vary over time (i.e., the surface area is not kept substantially constant). In this embodiment the N-halogenated composition need not be placed in the skimmer basket, but may be maintained in contact with the recirculating water at any convenient location by placing the N-halogenated composition in a receptacle which allows the recirculating water to freely flow therethrough.

In one aspect of the present invention a method is provided for reducing the consumption of N-halogenated hydantoins when the same are used to treat recirculating water. For example, the use of prior art brominator chemical dispensing devices is difficult to regulate and results in an average consumption of 3 to 5 pounds of bromochlorodimethylhydantoin per week per 10,000 gallons. In contrast, the skimmer-fed application of tableted bromochlorodimethylhydantoin accompanied by the biweekly addition of cationic polymeric compounds results in an average BCDMH consumption rate of only 1 to 2 pounds per week per 10,000 gallons.

As to the compositions themselves, the N-halogenated hydantoin is preferably of the formula:

$$\begin{array}{c|c}
R_1 & R_2 \\
N & X
\end{array}$$

-6-

where:

5

10

15

20

25

30

35

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a lower (C_{1-8}) alkyl, a lower (C_{1-8}) acyl, or a lower (C_{1-8}) alkoxy; and

 $\rm R_1$ and $\rm R_2$ are each $\rm C_{1-8}$ mono- or multivalent hydrocarbon radicals of the group consisting of alkyl and/or saturated or unsaturated monocyclic hydrocarbon radicals having five or six carbon atoms per cycle, which radicals can be substituted with lower alkyl, lower acyl, lower alkoxy, carboxy and/or sulfonic acid groups.

As previously indicated, bromochlorodimethylhydantoin is preferably used. Other N-halogenated hydantoins with higher order straight or branched chain alkyl groups in Position 5 of the heterocyclic imidazolidinedione ring may be more or less desired according to the particular characteristics desired to be achieved, and according to other technical and economic considerations.

The N-halogenated hydantoin may be provided in either dry or liquid form. When provided as a dry composition, the hydantoin may be agglomerated, compressed, extruded or tableted into essentially any size or shape. Preferably, the N-halogenated hydantoin is formed into tablets weighing from 1 to 500 grams. More preferably, the N-halogenated hydantoin is provided as an agglomerated, compressed, extruded or tableted product of undefined dimension, size and/or shape weighing from 10 to 200 grams. Most preferably, the N-halogenated hydantoin is provided as an agglomerated, compressed, extruded or tableted product of undefined dimension, size and/or shape weighing from 20 to 125 grams. The N-halogenated hydantoin used in certain of the following examples was provided as a 1" diameter, 20 gram compressed tablet or a 2 3/4" diameter, 120 gram compressed puck.

In one preferred embodiment of the present invention,

10 .

15

20

25

30

35

one or more pucks of bromochlorodimethylhydantoin agglomerate are placed directly in the skimmer basket of a pool. The pucks are allowed to dissolve in the pool water over a period of between about three days and about seven days before new pucks are added to the skimmer basket to replenish the supply. In this embodiment of the invention the agglomerate is provided in an amount and in a form such that the surface area of the agglomerate exposed to the water changes over time as the pucks dissolve, and is not substantially constant.

In another preferred embodiment the N-halogenated hydantoin is delivered to the recirculating water via a device which holds the hydantoin and is placed in the recirculating water flow. For example, the N-halogenated hydantoin may be placed in a reusable or a disposable container which holds the hydantoin while simultaneously allowing water to flow freely therethrough. The container is preferably corrosion resistant, and may be an interlocking clam shell device, or a twist-open or permeable mesh bag-type assembly. The receptacle may be maintained in contact with the water at essentially any location in the pool or its associated plumbing. Most preferably, the receptacle is placed in the skimmer basket.

The total halogen is preferably between 0.1 and 10.0, expressed as mg/liter $\rm Br_2$. More preferably, total halogen is between 0.25 and 2.5 mg/liter $\rm Br_2$. In one preferred embodiment the total halogen is between 0.40 to 0.80 mg/liter $\rm Br_2$.

In one preferred embodiment of the present invention, a secondary composition is provided to the pool water to work in conjunction with the bromochlorodimethylhydantoin. In the most preferred of these embodiments the bromochlorodimethylhydantoin agglomerate is delivered through the skimmer basket technique previously described, and the secondary composition is added directly to the

-8-

pool. The secondary composition is preferably added to the pool at least once a month, more preferably every ten to twenty days, and most preferably biweekly.

The secondary composition preferably exhibits properties such as water clarification, halogen residual stabilization, etc., in circulating water systems. Preferably the secondary composition is a polymer; most preferably a cationic polymer. Polymeric and/or non-polymeric substances that are rigid, water soluble clarifying agents in any physical form such as aluminum sulfate, ferric salts, iron III compounds, etc., may advantageously be used.

5

10

15

20

25

30

35

also be used.

In certain preferred embodiments the secondary composition is a water soluble cationic polymer such as poly(hexamethylammonium chloride), poly(dodecamethylenedimethylimino chloride), poly[(oxyethylene dimethylimino) ethylene-(dimethylimino) ethylene dichloride], 1,3-diaza-2,4-cyclopentadiene (with 1-chloro-2,3-epoxypropane to assist in water clarification and filtration), polyvinyl amine, chitosan, polyethylene amine or a polymer of 1,6-hexanediamine-N,N,N',N'-tetramethyl. Alternatively, the fluoride, chloride, or bromide salts of these compounds may

The molecular weight of the cationic polymer is preferably between about 500 Da to 100,000 Da, with polymers having a molecular weight of between about 1,000 Da and 20,000 Da being most preferred.

The cationic polymer is preferably provided at a concentration of about 0.10 to 10.0 mg/liter as active cationic. More preferably, the polymeric cationics should be present in a concentration of about 0.75 to 7.5 mg/liter as active cationic. Most preferably, the polymeric cationics should be present in a concentration of about 1.0 to 4.0 mg/liter as active cationic.

Reference will now be made to specific examples using

5

10

15

20

25

the processes described above. It is to be understood that the examples are provided to more completely describe preferred embodiments, and that no limitation to the scope of the invention is intended thereby.

Examples 1 through 4

The field performance of prior art methods of delivering bromochloro-5,5-dimethylhydantoin was evaluated. The compound was delivered by placing 20 gram, 1" diameter tablets in a "brominator" chemical dispensing device.

The following information was recorded during each pool visit. (1) Date and time of pool inspection; (2) pH; (3) total alkalinity as mg/l CaCO₃; (4) calcium hardness as mg/l CaCO₃; (5) observed total bromine residual as ppm bromine; (6) water temperature (F°); (7) total dissolved solids; (8) copper and iron content; (9) cyanuric acid (Stabilizer) content as mg/l cyanuric acid; (10) turbidity as NTU's; (11) pounds of N-halogenated compound added; (12) Brominator Chemical Dispensing Device setting; and (13) general pool appearance (visual).

The test period was June-September, with most pools being tested weekly over a 12-15 week period.

EXAMPLE 1

The system represented in Example 1 is a 14,770 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filtering system and a pump. The pool was equipped with an AQUABROME® Brominator Chemical Dispensing device CR8.19AT plumbed in a pressure-suction configuration. The pool operated approximately 12 hours per day.

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.7 pounds

-10-

per week per 10,000 gallons. The average observed turbidity ranged between 0.05 and 0.49, with an average observed turbidity of 0.17 for the trial period. The average observed total residual bromine was 1.48 ppm. No algae formation was observed during the test period.

5

10

15

20

25

EXAMPLE 2

The system represented in Example 2 is a 21,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a high rate sand filter and a pump. The pool was originally treated with stabilized chlorine (e.g., trichloro-s-triazinetrione) via skimmer feed, but was fitted with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction configuration. The pool operated approximately 12 to 14 hours per day.

During the trial period the average consumption rate of tableted Bromochloro-5,5-dimethylhydantoin was 5.0 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.06 and 0.47, with an average observed turbidity of 0.19 for the trial period. The average observed total residual bromine was 1.59 ppm. No algae formation was observed during the test period.

EXAMPLE 3

The system represented in Example 3 is a 21,500 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a high rate sand filter and a pump. The pool was equipped with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction configuration. The pool operated routinely from 12 to 24 hours.

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.43 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.43, with an average observed

10

25

30

turbidity of 0.20 for the trial period. The average observed total residual bromine was 1.46 ppm. No algae formation was observed during the test period.

EXAMPLE 4

The system represented in Example 4 is a 15,400 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a cartridge filter system and a pump. The pool was fitted with an AQUABROME® Brominator Chemical Dispensing Device CR8.19AT plumbed in a pressure-suction configuration. The pool operated routinely from 12 to 24 hours per day.

During the trial period the average consumption rate of tableted bromochloro-5,5-dimethylhydantoin was 4.35 pounds per week per 10,000 gallons.

It can be seen from the above that the methods of the prior art provide bromochlorodimethylhydantoin to swimming pool water at an average consumption rate of about 4.2 pounds per week per 10,000 gallons for outdoor residential swimming pools of between about 10,000 and about 25,000 gallons. The average observed turbidity ranged between 0.09 and 0.49, with an average observed turbidity of 0.26 for the trial period. The average observed total residual bromine was 4.01 ppm. No algae formation was observed during the test period.

Examples 5 through 14

Test pools were treated with compressed pucks containing bromochloro-5,5-dimethylhydantoin agglomerate as the active ingredient via skimmer-fed application, and by the direct biweekly addition of 200 ml of a cationic polymeric compound (specifically, poly[hexamethylammonium] chloride) per 10,000 gal. of pool water. The consumption of bromochlorodimethylhydantoin was reduced without sacrificing water quality.

-12-

EXAMPLE 5

The system represented in Example 5 is a 29,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and a pump. The pool operated routinely for 12 hours per day, and was facilitated by a timer.

During the trial period the average consumption of BCDMH was 1.39 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.58, with an average observed turbidity of 0.23 for the trial period. The average observed total residual bromine was 0.57 ppm. No algae formation was observed during the test period.

EXAMPLE 6

The system represented in Example 6 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filter, and a pump. The pool operated approximately 12 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 0.98 pound per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.60, with an average observed turbidity of 0.24 for the trial period. The average observed total residual bromine was 0.60 ppm. No algae formation was observed during the test period.

25 EXAMPLE 7

5

10

15

20

30

The system represented in Example 7 is a 10,000 gallon, outdoor pool. This pool is a vinyl-lined, above-ground system equipped with a makeshift sand filter, and a 1.5 horsepower pump. The pool operated approximately 18 hours per day and was not equipped with a timer.

During the 14-week trial period the average consumption of BCDMH was 0.72 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.14 and 0.55, with an average observed turbidity of 0.30 for the trial period. The average observed total residual bromine was 0.31 ppm. No algae formation was observed during the test period.

EXAMPLE 8

The system represented in Example 8 is a 27,000 gallon, outdoor pool. This pool is a plaster in-ground system equipped with a cartridge filter and a 1.5 horsepower pump. The pool operated approximately 24 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.45 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.10 and 0.31, with an average observed turbidity of 0.16 for the trial period. The average observed total residual bromine was 1.49 ppm. No algae formation was observed during the test period.

20

25

30

15

EXAMPLE 9

The system represented in Example 9 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a 1.5 horsepower pump. The pool operated approximately 12 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.10 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.08 and 0.51, with an average observed turbidity of 0.32 for the trial period. The average observed total residual bromine was 0.63 ppm. No algae formation was observed during the test period.

-14-

EXAMPLE 10

The system represented in Example 10 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a 0.75 horsepower pump. The pool operated approximately 24 hours per day and was not equipped with a timer.

5

10

15

20

25

During the trial period the average consumption of BCDMH was 1.93 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.09 and 0.56, with an average observed turbidity of 0.29 for the trial period. The average observed total residual bromine was 1.17 ppm. No algae formation was observed during the test period.

EXAMPLE 11

The system represented in Example 11 is a 32,500 gallon, outdoor pool. This pool is a plaster, in-ground system equipped with a D.E. filter, and a 1.0 horsepower pump. The filtration system operated approximately 10 hours per day and was equipped with a timer.

During the 14-week trial period the average consumption of BCDMH was 1.05 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.11 and 0.37, with an average observed turbidity of 0.17 for the trial period. The average observed total residual bromine was 0.59 ppm. No algae formation was observed during the test period.

EXAMPLE 12

The system represented in Example 12 is a 15,100 gallon outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a filter and a pump. The pool operated

15

20

25

30

approximately 24 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 1.02 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.14 and 0.60, with an average observed turbidity of 0.25 for the trial period. The average observed total residual bromine was 0.71 ppm. No algae formation was observed during the test period.

EXAMPLE 13

The system represented in Example 13 is a 27,000 gallon, outdoor pool. This pool is a plaster, in-ground system equipped with a D.E. filter and a pump. The pool operated approximately 10 hours per day and was not equipped with a timer.

During the trial period the average consumption of BCDMH was 1.69 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.07 and 0.18, with an average observed turbidity of 0.11 for the trial period. The average observed total residual bromine was 1.38 ppm. No algae formation was observed during the test period.

EXAMPLE 14

The system represented in Example 14 is a 20,000 gallon, outdoor pool. This pool is a vinyl-lined, in-ground system equipped with a sand filter and a pump. The pool operated approximately 24 hours per day and was equipped with a timer.

During the trial period the average consumption of BCDMH was 1.08 pounds per week per 10,000 gallons. The average observed turbidity ranged between 0.06 and 0.61, with an average observed turbidity of 0.33 for the trial period. The average observed total residual bromine was 0.77 ppm.

-16-

No algae formation was observed during the test period.

5

10

15

20

25

30

It can be seen from the above that the present invention provides for more finely tuned product delivery rate facilitating a more efficient use of N-halogenated compound than can be obtained by prior art delivery methods. example, Examples 1 through 4 show that the tested outdoor pool systems using a Brominator Chemical Dispensing Device as directed in Paterson Patent No. 3,412,021 had an average consumption of about 4.6 pounds of tableted Bromochloro-5,5-dimethylhydantoin per week per 10,000 gallons. In contrast, examples 5-14 show that the tested outdoor pool systems using the skimmer-fed application of tableted Bromochloro-5,5-dimethylhydantoin and the biweekly addition of cationic polymeric compounds resulted in average consumption rate of about 1.2 pounds per week per 10,000 gallons. This is a significant advantage that was not taught or suggested by the prior art.

It can also be seen that water quality was maintained with the inventive skimmer-feed method. In particular, Examples 1 through 4 show that the tested outdoor pool systems using a Brominator Chemical Dispensing Device had an average observed turbidity of 0.21, while examples 5-14 show that the tested outdoor pool systems using the skimmer-fed application of tableted bromochlorodimethylhydantoin and the biweekly addition of cationic polymeric compounds resulted in average observed turbidity of 0.24.

Finally, it can be seen that the skimmer-fed systems of the present invention effectively inhibited algae growth, even when operating at lower-than-conventional total bromine residuals. In particular, effective algae inhibition was observed at residual bromine levels of less than 1.5 ppm, and more particularly at residual bromine levels of less than 1.0 ppm, including at residual bromine levels as low as about 0.3 ppm. The prior art does not teach or suggest

-17-

that effective algael inhibition can be obtained at these low residual bromine levels when bromochlorodimethylhydantoins are used.

EXAMPLE 15

5 The Table below shows bactericidal performance when bromochloro-5,5-dimethylhydantoin is applied at lower residual bromine concentrations. The average bromine residual for examples 6-14 is 0.73 mg/liter. These extremely low bacterial counts provide further support to the proposition that lower residuals of bromochloro-5,5-Dimethylhydantoin are effective in controlling the propagation of bacterial and microbiological contaminants.

TABLE

13	Microbiological	Results	(CFU'
13	Microbiological	Results	(CFU

	Example No.	10°	10-1	10-2	10-3
	6	CNR	CNR	0	11
	7	0	0	0	0
20	8	CNR	CNR	CNR	0
	9	0	. 0	0	0
	10.	0	0	. 0	0
	11	0	0	· 0	0
	12	0 .	. 0	0	0
25	13	0	0	0	0
	14	0	0	0	0
1	15	0	0	0	0

CNR - Cannot Read

-18-

Examples 16-19 represent test pools that were treated with compressed pucks containing bromochloro-5,5-dimethylhydantoin agglomerate as the active ingredient via skimmer-fed application, without the additional use of a cationic polymer. The consumption of bromochlorohydantoin was reduced without sacrificing water quality.

5

10

15

20

25

30

EXAMPLE 16

The system represented in Example 16 is an 18,400 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.09 pounds per week per 10,000 gallons. The average observed turbidity was between 0.06 and 0.21, with an average observed turbidity of 0.10 for the trial period. The average observed total residual bromine was 0.39 ppm. The average observed cationic polymer concentration was 0.40 ppm. No algae formation was observed during this period.

EXAMPLE 17

The system represented in Example 17 is an 18,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.70 pounds per week per 10,000 gallons. The average observed turbidity was between 0.06 and 0.25,

-19-

with an average observed turbidity of 0.10 for the trial period. The average observed total residual bromine was 0.92 ppm. The average observed cationic polymer concentration was 0.48 ppm. No algae formation was observed during this period.

EXAMPLE 18

The system represented in Example 18 is a 22,000 gallon, outdoor pool. The pool is a vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.35 pounds per week per 10,000 gallons. The average observed turbidity was between 0.05 and 0.18, with an average observed turbidity of 0.11 for the trial period. The average observed total residual bromine was 1.25 ppm. The average observed cationic polymer concentration was 0.40 ppm. No algae formation was observed during this period.

20

25

30

10

15

EXAMPLE 19

The system represented in Example 19 is a 16,000 gallon, outdoor pool. The pool is vinyl-lined, in-ground system equipped with a sand filter and pump. The pool operated routinely for 24 hours per day and was not equipped with a timer.

During the trial period, the average consumption rate of tableted BCDMH was 1.28 pounds per week per 10,000 gallons. The average observed turbidity was between 0.45 and 0.11, with an average observed turbidity of 0.20 for the trial period. The average observed total residual bromine was 0.85 ppm. The average observed cationic polymer concentration

-20-

was 0.42 ppm. No algae formation was observed during this period. $\ \ \,$

In view of the above it can be seen that with the methods of the present invention substantially lower residuals of bromine concentration may be used to effectively sanitize swimming pool water when bromochlorodimethylhydantoin is applied via the skimmer-fed application described herein.

While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes and modifications that come within the spirit of the invention are desired to be protected.

10

15

-21-

CLAIMS

What is claimed is:

1. A method of treating the water of a swimming pool equipped with a skimmer basket, comprising the steps of:

(a) putting into the skimmer basket an N-halogenated hydantoin of the formula:

$$0 \longrightarrow N \longrightarrow N \longrightarrow N$$

where:

10

15

20

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a C_{1-8} alkyl, a C_{1-8} acyl, or a C_{1-8} alkoxy; and

 $m R_1$ and $m R_2$ are each independently a $m C_{1-8}$ monovalent or multivalent hydrocarbon radical selected from the group consisting of alkyl hydrocarbon radicals and saturated or unsaturated monocyclic hydrocarbon radicals having five or six carbon atoms per cycle; wherein said radicals are optionally substituted with one or more substituents selected from the group consisting of $m C_{1-8}$ alkyl, $m C_{1-8}$ acyl, $m C_{1-8}$ alkoxy, carboxy and sulfonic acid groups; and

(b) allowing a substantial portion of the N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the skimmer basket.

- 2. The method of claim 1 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.
 - The method of claim 1 wherein said N-halogenated

-22-

compound is provided as an agglomerate, and wherein said "allowing" step comprises allowing a substantial portion of the agglomerate to dissolve before replenishing the supply of agglomerate in the skimmer basket.

- The method of claim 1 wherein said N-halogenated compound is provided to the skimmer basket by placing the N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.
- 5. In a method of treating the water of a swimming pool equipped with a skimmer basket, wherein the swimming pool water is treated with both an N-halogenated compound and an additional water clarifying composition, the improvement comprising providing the N-halogenated compound to the pool water by placing the N-halogenated compound in the skimmer basket and allowing a substantial portion of the N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the skimmer basket.
- 6. The method of claim 5 wherein said additional water clarifying composition is a cationic polymer.
 - 7. The method of claim 5 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.
 - 8. The method of claim 6 wherein said cationic polymer is added to the water biweekly.
- 9. The method of claim 5 wherein said N-halogenated compound is provided to the skimmer basket by placing the N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.

- 10. A method of treating the water of a swimming pool equipped with a skimmer basket, said method comprising the step of providing an N-halogenated compound to the skimmer basket of a swimming pool in an amount and form effective to provide between about 0.2 and 1.0 ppm of the N-halogenated compound to the water.
- 11. The method of claim 10 wherein said N-halogenated compound is a bromochlorodimethylhydantoin.
- 12. The method of claim 10, and additionally including
 10 the step of providing a secondary composition to the pool
 water to work in conjunction with the N-halogenated
 composition; wherein said secondary composition is provided
 to the pool water by placing the secondary composition
 directly in the pool water.
- 15 13. The method of claim 12, wherein said secondary composition is a cationic polymer.
- 14. The method of claim 10 wherein said N-halogenated compound is provided to the skimmer basket by placing the N-halogenated compound in a container effective to allow water to flow therethrough, and placing said container in the skimmer basket.
 - 15. A method of treating a recirculating water system, said method comprising the steps of:
- (a) contacting the recirculating water with an N-halogenated hydantoin of the formula:

where:

X is chlorine, bromine or iodine;

Y is chlorine, bromine, iodine, hydrogen, a $\rm C_{1-8}$ alkyl, a $\rm C_{1-8}$ acyl, or a $\rm C_{1-8}$ alkoxy; and

R₁ and R₂ are each independently a C₁₋₈ monovalent or multivalent hydrocarbon radical selected from the group consisting of alkyl hydrocarbon radicals and saturated or unsaturated monocyclic hydrocarbon radicals having five or six carbon atoms per cycle; wherein said radicals are optionally substituted with one or more substituents selected from the group consisting of C₁₋₈ alkyl, C₁₋₈ acyl, C₁₋₈ alkoxy, carboxy and sulfonic acid groups; and

(b) allowing a substantial portion of the N-halogenated hydantoin to dissolve before replenishing the supply of N-halogenated hydantoin in the recirculating water.

INTERNATIONAL SEARCH REPORT

International application No. PCT/US97/08712

	FICATION OF SUBJECT MATTER				
IPC(6) :CO2	IPC(6) :CO2F 1/50				
	emational Patent Classification (IPC) or to be	oth national classification and IPC			
	SEARCHED				
	entation scarched (classification system follow	wed by classification symbols)			
i .	U.S. : 210/712, 721,725, 728, 732, 734, 735, 736, 755, 764, 765; 162/161; 504/156, 158				
Documentation so NONE	earched other than minimum documentation to	the extent that such documents are included	d in the fields searched		
Flectmaic data h	ase consulted during the international search	(name of data have and sub			
NONE	and constitute during the international scarcif	(maine of data base and, where practicable	, search terms used)		
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where	appropriate, of the relevant passages	Relevant to claim No.		
	3,412,021 A (PATERSON ET E ENTIRE DOCUMENT	AL) 19 NOVEMBER 1968,	1-3, 5, 7, 10, 11, 15		
			1-3, 5, 7, 10- 12, 15		
Y US	4,530,120 A (ETANI) 23 CUMENT	JULY 1985, SEE ENTIRE	4, 6, 8, 9, 12- 14		
Further doc	uments are listed in the continuation of Box (C. See patent family annex.			
•	gories of cited documents:	"T" later document published after the inter date and not in conflict with the applica	mational filing date or priority		
	efining the general state of the art which is not considered ticular relevance	principle or theory underlying the inve	ntion		
L* document w	ment published on or after the international filing date hich may throw doubts on priority claim(s) or which is	"X" document of particular relevance; the considered novel or cannot be considered when the document is taken alone	claimed invention cannot be ed to involve an inventive step		
special reas	ablish the publication date of another citation or other on (as specified)	"Y" document of particular relevance; the considered to involve an inventive :	claimed invention cannot be		
mens	eferring to an oral disclosure, use, exhibition or other	combined with one or more other such being obvious to a person skilled in the	documents, such combination		
the priority o	blished prior to the international filing date but later than date claimed	'&' document member of the same patent for			
28 JULY 1997	completion of the international search	Date of mailing of the international sear 1 9 AUG 1997	ch report		
lame and mailing a	address of the ISA/US	Authorized officer //			
Commissioner of Pa Box PCT	itents and Trademarks	Heli ve	/hor		
Washington, D.C.		PETER A. HRUSKÓCI (191			
acsimile No. (70	03) 305-3230	Telephone No. (703) 308-3839			

THIS PAGE BLANK (USPTO)